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Advances in the Preparation of Uncopyable Photoluminescent Security Inks from Long-Persistent Phosphors for Secure Documents

Marwa M. Abdelhameed [1], Yasser A. Attia [1], Meram S. Abdelrahman [2], Tawfik A. Khattab [2,*]

[1] *Department of Laser in Meteorology, Photochemistry & Agriculture, National Institute of Laser Enhanced Sciences, Cairo University, Giza 12613, Egypt*

[2] *Dyeing, Printing and Auxiliaries Department, National Research Centre, Cairo 12622, Egypt*

Abstract

Luminescent security inks have great commercial importance in anti-counterfeiting applications. There are many methods and strategies for making luminescent ink and the improvement for these methods and designing strategies is the major challenge. Luminescent inks are usually characterized with high stability, low cost of ink medium, availability of ink medium, high-quality distribution of luminescent nanomaterials, strong luminescence intensity, the suitability of the print on different surfaces, high surface tension, and viscous nature of ink medium. Luminescent security inks may be hydrophilic or hydrophobic in nature so studying chemistry for this kind of ink is very important before using it to print security encodings and patterns on various kinds of surfaces. There are principles to synthesize luminescence-based security inks with desired characteristics, such as the selection of photoluminescent ink medium. Thus, we must take into consideration some conditions for the ink medium, including homogeneous dispersion of the luminescent nanomaterials, viscous medium appropriate to print onto various types of printable surfaces, and appropriate boiling point of the ink medium. In this review, we discuss the recent developments on hybrid photochromic inks for anticounterfeiting applications.

Keywords: Long-persistent phosphors; Security inks; Anticounterfeiting; Documents.

1. Introduction

Documents have an important value in our daily life. It has been used in many fields, such as financial, business, legal, social affairs [1]. The definition of document is not limited to a paper sheet containing handwriting or computer-prepared text, but it is any material enclosing marks, signs or symbols, so the document can be presented on paper by using either electronic or mechanical methods or by handwriting employing pens or pencils and also can be presented on many other surfaces by using other instruments [2]. The protection of valuable documents from the forgery is very important for public safety. There are three different types of documents, including secret, private and public documents. Secret documents are any material contains sensitive information, controlled by law and must be protected, for access to these documents requires government approval, mishandling of these documents leads to criminal penalties. Private documents are materials that contain information related to an individual or a group to isolate themselves, this information differs according to cultures and individuals [3]. The private information of any person that means this information is sensitive to him. There is an affinity in the meaning between security and privacy so the protection of the private document is important. Public documents are materials that contain public information [4]. Not all documents are question documents, but only the falsified ones which contain uncertain information are considered as questioned documents. The questioned documents can be prepared by using many types of materials [5]. Sometimes these materials raise doubt and include fraud even though it fully corresponds to the document's history and purpose and that leads to making it may be challenged. The process of forensic examination for questioned documents is a scientific examination for documents, takes place by forensic document examiner (FDE) for documents which subjected to counterfeiting [1]. Determination the authenticity of documents is very important. FDE helps the court to find solutions for document problems related to its preparation, treatment and history. He or she must be a scientist more than technical and aware of the methods used for

*Corresponding author e-mail: ta.khattab@nrc.sci.eg; (Tawfik A. Khattab).

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determining the facts in documents by making a comparison between the questioned documents and the known standard. The rule of FDE not only the identification of handwriting and printed matter but also analysis for the document components which representative in inks, papers and that to discover the counterfeiting which takes place in the documents such as addition and substitution, restoring the erased and obliterated writing. Then the report about the resulted opinion is prepared by a language that can be understood by a layperson who may be a judge or other concerned bodies [6]. In the current review article, recently developed photochromic printing inks were discussed for security applications.

1. Photoluminescence activity

Dyes and pigments have been reported as functional compounds able to impart colors to materials, such as paper sheets and textiles [7-18]. Chromic colorants have the ability to provide variable chromogenic properties when exposed to external stimuli, such as heat and light [19-31]. Chromic colorants were employed in countless applications, such as sensors, anticounterfeinting and bioimaging *[32-56]*. Luminescence is a phenomenon at which the luminescent materials (phosphors) emit light after exposure to an excitation light source. There are different ways for classification of the luminescent materials [57-59]. a- Types of luminescent materials according to the type of excitation light source: Photoluminescent, X-ray luminescent, cathodoluminescent, thermoluminescent, bioluminescent, cathodoluminescent, chemiluminescent, electroluminescent, triboluminescent, and sonoluminescent [60, 61]. Al-Qahtani and coworkers reported recently the authentication of documents employing lanthanide-doped aluminate nanoparticles immobilized into polypropylene electrospun nanofibers [45]. Using the sol-gel method, the same research group also reported the preparation of photochromic smart glass with improved hydrophobicity and UV shielding. The photoluminescent glass showed two emission bands at 427 and 522 nm associated with an excitation band at 371 nm. Results demonstrated that the photoluminescence colorless glass substrates have improved hydrophobicity and UV shielding [48].

Khattab et al. [53] reported recently the use of the simple solution blowing spinning technology to develop photochromic dual-mode authentication nanoscale fibers from cellulose nanowhiskers-supported polyacrylonitrile **(Figure 1)**.

Types of luminescent materials according to their chemical family and application include organic pigments, inorganic phosphors, semiconductors, highlighting fluorescent proteins, and metal complex [59-64]. There is a great challenge for the improvement and enhancement of the optical properties of luminescent materials. Khattab et al. reported recently the preparation of long-persistent photoluminescent spray-coated paper [50]. Simple formulation was prepared from an organic-inorganic composite to provide a transparent spray-coated film onto paper surface. The coated layer showed an excitation wavelength at 365 nm associated with an emission wavelength at 517 nm, demonstrating a color change to green under ultraviolet light with high stability **(Figure 2)**.

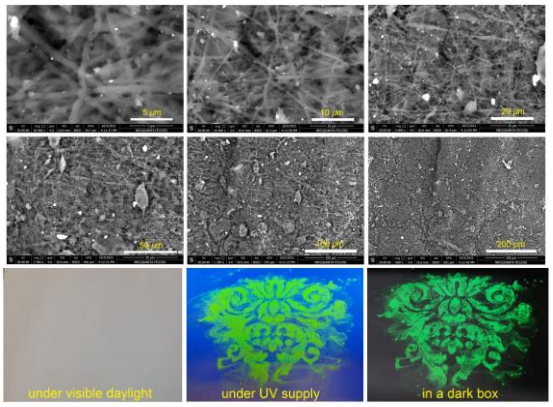

Figure 1. SEM images of nanofibrous film (*top*), and photochromism displaying colorimetric change from off-white under daylight to green under ultraviolet light and greenish-yellow in the dark (*bottom*) [53]. "Reprinted with permission from {Khattab et al. *Cellulose* 2022}. Copyright {2022} *Elsevier*."

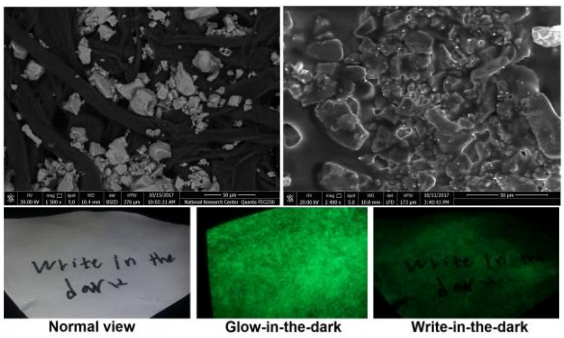

Figure 2. SEM images (*top*), and color change (*botton*) of spray-coated paper sheet [50]. "Reprinted with permission from {Khattab et al. *Carbohydrate polymers* 2018}. Copyright {2018} *Elsevier*."

Most of the luminescent materials are inorganic, the synthesis methods for these materials especially strontium aluminate ($SrAl_2O_4$) based materials and studying the relation between the structures of these materials and the photoluminescent behavior will be discussed below. The first part shows an introduction about inorganic luminescent materials and gives brief knowledge about their characterization methods. The second part discusses in detail the synthesis methods of $SrAl_2O_4$, including microemulsion, co-

precipitation, combustion, hydrothermal, and sol-gel approaches [57-59]. There is a challenge to develop the synthesis methods of luminescent materials to obtain sub- micrometric particles with low cost and avoid stringent, intricate, tedious, toxicity and elemental scarcity. By using the molten salt synthesis process $SrAl_2O_4$ based materials in sub-micrometric size were obtained, these particles have a large response toward the photoluminescence. The third part includes discussions about the relation between synthesis processes of luminescent materials and its photoluminescence activity; also it discusses the existing challenges for improvement and enhancement of the photoluminescence phenomenon and gives some conclusions. The final part includes some applications of photoluminescent materials in the field of luminescent markers [58].

2. Photoluminescent security inks

There are different types of photoluminescent security inks by using different photoluminescent nanomaterials, such as rare-earth photoluminescent nanomaterials, dual-mode, upconversion, downconversion, plasmonic nanomaterials, metal-organic frameworks and quantum dots [65].

2.1. Lanthanide-doped nanomaterials

Lanthanide-doped photoluminescent nanomaterials have remarkable optical properties usable for vaious applications, such as luminescent security inks, optoelectronics, bio-imaging security applications, optical displays and sensors. Lanthanide based luminescent security inks exhibit many features. Irradiation of it to UV excitation light source leads to the production of visible emission and that makes it used in anti-counterfeiting applications compared to fluorescent inks. It exhibits in a single lattice both upconversion and downconversion processes so that it is complicated to photocopy as compared to standard fluorescent inks. It has sharper transitions without photobleaching compared to fluorescent inks. Due to the above features, lanthanide-based luminescent inks provide the accurate color rendering index by exposure to definite excitation light source has definite power densities and that makes it hard to photocopy the authenticated reading [61].

2.1.1. Downconversion nanomaterials

The synthesis of downconversion inks uses Y_2O_3:Eu^{3+} nanoscale particles, employing the sodium salt of hexametaphosphate dissoluted in deionized water followed by the addition of Y_2O_3: Eu^{3+} particles (500 mg) to the sodium hexametaphosphate aqueous solution (30 mL) with constant stirring for 15 minutes. Then, ethanol (5 mL) was added to the produced admixture, which was maintained in an ultrasonic bath for 60 minutes. Lastly, the capped nanoparticles were collected by ultracentrifugation. An amount of the produced mixture (0.2 mg cm^{-3}) was dispersed in deionized water at ambient conditions to introduce an aqueous luminescence-based ink with high stability and transparency [66].

2.1.2. Upconversion nanomaterials

The synthesis of upconversion security ink was suggested by Blumental and co-workers by employing toluene as the ink medium solvent. A 2 wt% of $NaYF_4$:Er,Yb (upconversion nanoparticles) were dispersed in toluene, followed by the addition of poly(methyl methacrylate) (1 wt%) together with sufficient amount of methylbenzoate. Then we used synthesized ink in direct-write and screen printing practices. There is another method established by Meruga et al. to synthesize green and blue security inks employing $NaYF_4$:Er,Yb and $NaYF_4$:Tm,Yb, respectively, which are upconversion nanoparticles used in printing QR codes [67, 68]. Nanophosphor and poly(methyl methacrylate) beads were added to a mixture of methylbenzoate and toluene (10:90 v/v). Then, strong stirring followed by sonication afforded a homogenous dispersion of nanoparticles and the full dissolution of polymers. Hydrophilic and hydrophobic inks based on β-$NaYF_4$: Er, Yb (upconversion nanoparticles) were established. To synthesize a hydrophobic ink with ideal surface tension and viscosity, the upconversion nanoscale particles were added into a mixture of glycerol trioleate and cyclohexane. On the other side, to synthesize a hydrophilic ink, the upconversion particles were added into a mixture of glycerol and ethanol. Sodium dodecyl sulfate (3 mg/L) was included in the hydrophilic ink to optimize the surface tension [67].

2.1.3. Dual-mode photoluminescent nanomaterials

The synthesis strategy of dual-mode photoluminescent inks is by using the PVC/Au medium which is commercially available. In this method, dual-mode nanoscale particles were dispersed in polyvinyl chloride/gold medium, and homogenized (45 kHz) to provide good dispersion. The synthesized ink was successfully employed in a screen-printing technique to print various images and security encoding [61].

2.2. Quantum dots (QD) inks

CdTe QD/branched polyethyleneimine was employed by Lu et al. as security ink, suggesting a multicolor rewritable fluorescent ink. The obtained fluorescent design can be easily erased by using a drop of polyethyleneimine, leading to decomposition of surface an printed layer of QD [69].

2.3. MOF luminescent security ink

Metal-organic frameworks(MOF)-based photoluminescent inks were established for inkjet printing. Luz et al. reported a simple and cheap

strategy for placing of MOF-based luminescent film onto flexible substrates, such as paper and plastic sheets [70].

2.4. Plasmonic nanomaterials

Campos-Cuerva et al. established a strategy for the development of security luminescent ink using metallic nanoscale particles as anticounterfeiting tags, which can be screen-printed onto various classes of papers sheets. This metallic nanoparticle-based ink was synthesized by the addition of oil-based or water-based varnishes to gold nanorods, silver nanoparticles.

3. Printing methods

3.1. Screen-printing

The screen-printing technique is transferring inks onto the substrate by using mesh except for the impermeable areas to ink using a blocking stencil. The mesh apertures of the screen filled with ink when squeegee is moved crosswise the stencil screen, the screen touch the substrate and wet it by ink by making a reverse stroke. Through the screen printing technique, we can use the synthesized ink to print security patterns. Plasmonic nanoparticles based inks can be screen-printed onto various types of paper sheets as established by Campos-Cuerva et al. [61].

3.2. Aerosol-jet printing

This technique depends on using the aerodynamic focusing in the colloidal suspensions for making a high-resolution deposition. Aerosol jet printing techniques can be used to print QR patterns onto paper sheets by green and blue upconversion nanoparticles. This method was established by Meruga et al. [71].

3.3. Inkjet printing

This technique is an ejection process of ink from a nozzle. An external voltage is applied to the ink chamber and that cause sudden reduction leads to formation a shockwave in the ink and makes ink drop eject from the nozzle, by the action of gravity and the air resistance the ejected drop falls until it touches the surface of the substrate [72]. After spreading the drop on the substrate surface. The printing technique depends on two parameters, the viscosity of used ink which is a function of polymer molar mass and the diameter of the dried ink drop which is a function of polymer concentration. The inkjet printing technique has many advantages so it used for printing security codes, such as high resolution and high luminescence security designs can be printed by using digital and flexible inkjet printing technique which established by You et al. [73]. The inkjet printing technique needs requirements that are important for determining its properties, these requirements are discussed in detail below. The dynamic viscosity, the surface tension of ink play a significant role in determining the efficiency of the inkjet printing technique. The printing resolution affected by the flow and the spreading of ink drops on the substrate. Contact angle (θc) is another important requirement for determining the efficiency of the inkjet printing technique because of it was responsible for the penetration of ink into substrates. It is the infinite angle between link drop and the substrates which comes from falling the ink droplet on a flat surface leading to partial wetting. Luminescence intensity and uniformity play a significant role in determining the efficiency of the printed patterns. They depend on the size of droplets ejected by the nozzle and their distribution on the substrate surface [67].

4. Inorganic long-persistent luminescence materials

The inorganic photoluminescent material classified according to the type of luminescence into two categories: fluorescent materials that have lifetime 10^{-9}–10^{-7} s and phosphorescent materials that have a higher life time [58, 74]. The emission of the luminescent materials is by one of these three things: an optical (luminescence) center, optical transition amid the related band states of host lattice or charge transfer. If the electronic states join in chemical bonding, there are many parameters that play a significant role in the determination of the emission spectrum as the bonding nature, a charge of ions, the distance between two neighboring ions and crystalline symmetry. There are two types for the electronic transitions:

(i) Intraconconfigurational d→ d (Mn^{2+}, Cr^{3+}) or 4f→4f (Eu^{3+}).

(ii) Interconfigurational (4f→5d transitions, Eu^{2+}, Ce^{3+}).

The selection rule states that transitions are spin forbidden but by resulting electric dipolar character transitions are partial allowed. In interconfigurational transition, it appears to allow transitions that have a broad emission band. The emission occurs by charge transfer by absorption of light energy, the transitions occur between electronic states, different kinds of orbitals or different ions [75, 76]. Phosphorescence or long-persistent photoluminescence is a light emission that stays for some time after removing the excitation light source. Bologna stone is the first phosphorescent material that contains some natural impurities has the ability to emits light. Many phosphorescent materials are developed during the last decades for giving emission cover all visible spectrums. There is a challenge to obtain long-lasting luminescence by development for about hundreds of phosphorescent material which has allowed during the experimental research [77]. Many strategies are used and the most common one is the German norm "DIN 67510-1: Photoluminescent pigments and

Products-Part 1: Measurement and marking at the producer" [78]. In this strategy the samples are exposed to Xe Arc Lamp (1000 1x) as an excitation light source for 10 min then the luminescence was measured after removing the excitation light source at 10,60 and 520 min. There is no standard method for defining and measuring the properties of phosphorescent materials [79-83]. Phosphorescent (persistent luminescent) materials comprise of the inorganic matrix(host)and dopant ions (activators). The activating ions (activators) is active centers, which could be rare earth elements or transition metal. These active centers function as traps (emitters) which stores the radiation absorbed by exposure to a certain excitation light source and emits this stored radiation by removing this light source. Nevertheless, the trapping mechanism for phosphorescent materials which has been studied has a strong disagreement. The chart contains data points that represent the chemical elements that have been used for doping the matrix (host). The doping process for a host can take place by one or more cations, and the emission color relies on the host material and dopants as shown in **Table 1**.

Table 1. showing the dependence of the emission color on the type of host material and dopant.

Host material type	**Dopant type**	**λ_{ex} (nm)**	**Emission color**
Zinc sulfide (ZnS)	Eu^{3+}	452	Blue light
Zinc sulfide (ZnS)	Cu^{+} or/and Co^{2+}	510	Green light
Zinc sulfide (ZnS)	Mn^{2+} and Ce^{2+}	570	Yellow light

Sulfides have good fluorescent properties but it represents phosphorescent properties by the synthesis methods and type of dopant. These compounds exhibit electroluminescent properties for light-emitting diodes (LEDs) and that makes it very important and attracts great interest. By doping ZnS with copper (Cu) and cobalt (Co) [84], the resulting material has attractive phosphorescent properties. Nevertheless, these materials have short persistent luminescence. Thus, radioactive elements like promethium and tritium have been used to obtain long-persistent photoluminescence. The using of radioactive materials increases the consumption of these materials but by the time the limitation of using radioactive elements reduces the using these materials. Calcium sulfides were activated with Eu^{2+}, Tm^{3+}, Ce^{+} and Bi^{3+} to emit red and blue lights, respectively. Strontium sulfide was activated with Eu^{2+} and Dy^{3+} to emit red light [85-87]. The above materials with their characteristic emissions had importance in the LED industry. Nevertheless, sulfides exhibit drawbacks as hygroscopic, low stability, not accepted in using as phosphorescent materials. Matsuzawa et al. discovered long-lasting afterglow material, this material is $SrAl_2O_4$:Eu^{2+}, Dy^{3+} [88]. $SrAl_2O_4$:Eu^{2+}, Dy^{3+} has brightness greater ten folds than ZnS:Co,Cu and that encourages the research in $SrAl_2O_4$. Doping aluminates (MAl_2O_4; M = Ca, Sr, Ba) with rare earth elements has been broadly studied. Doping of calcium aluminate with $Eu^{2+}$and Dy^{3+}, Nd^{3+} or B^{3+} leads to emission of light in the blue region [89, 90]. However, green emission was detected by doping with Mn^{2+} and Ce^{3+} [91]. By doping barium aluminates with Eu^{2+} and Nd^{2+} that leads to emission of light which has lifetime ca.7 but by doping it with Eu^{2+}, and Dy^{3+} the lifetime of the emitted light increases to 1h. Silicates system also exhibits the long afterglow time (i.e. >10h) As in $Sr_2MgSi_2O_7$ doped with Eu^{2+} and Dy^{3+} [92]. Silicates can be classified into two main categories: ($MSiO_3$) where (M) could be Ca, Ba, Cd or Mg; and ($M_2MgSi_2O_7$) where (M) could be Ca, Sr or Ba [93]. The oxides can be taken as luminescent materials, the lifetime of the emitted light is 1 hour [94]. There exist large number for phosphorescent materials; however, strontium aluminates are the most important one according to their advantages like brightness, stability and have the longest afterglow lifetime for the emitted light (>16h, threshold value: 0.3 cd/m^2). These materials used in many applications so many research studies take place on them; especially for $Sr_4Al_{14}O_{25}$, $SrAl_4O_7$, $SrAl_2O_4$ and $Sr_2Al_3O_6$ whose emission bands are blue, green, red respectively by doping them with Eu^{2+} and Dy^{3+}. As there are advantages there are drawbacks such as weak water resistance (i.e. Hydrolysis and deterioration for these materials by breaking the O-Sr-O bond). To overcome this drawback, the encapsulation method by using inorganic or organic layers is carried out. These layers prevent the hydrolysis of strontium aluminate but it decreases the luminescence intensity.

5. Strontium aluminate ($SrAl_2O_4$)

5.1. Structure description of strontion aluminate

There are two crystallographic structures for $SrAl_2O_4$:
(i) The monoclinic symmetry with space group P21, which is stable at temperature less than 650 °C.
(ii) Hexagonal symmetry with space group P6322, which is stable above 650 °C [95, 96].
In a reversible process, the monoclinic phase is directly transformed into the hexagonal phase and vice versa [97]. Ave et al. made a detailed study of the structural behavior of $SrAl_2O_4$ to solve this behavior [98]. Tridymite structure is complex so there is no accurate study by Raman spectroscopy about this structure. The theory group expects 81 active types for monoclinical phases and p21,20 and 61 active types for hexagonal phase, p6322 and p63

respectively [99]. Khattab et al. presented recently the preparation of electrospun nanofibrous-walled tubes as a potential product of luminescent endoscope, displaying glow in the dark chameleon effect **(Figures 3-5)** [32].

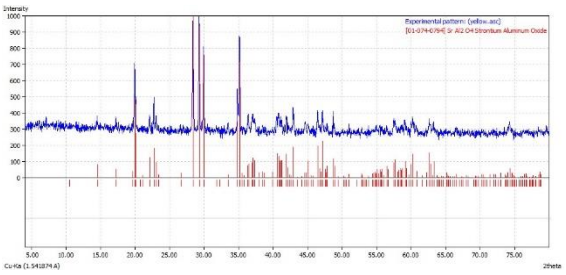

Figure 3. XRD pattern of lanthanide-doped $SrAl_2O_4$ nanoparticles (*top*), and its standard spectrum (JCPDS card No. 74-0794) (*bottom*) [32]. "Reprinted with permission from {Khattab et al. *Industrial & Engineering Chemistry Research* 2021}. Copyright {2021} *American Chemical Society*."

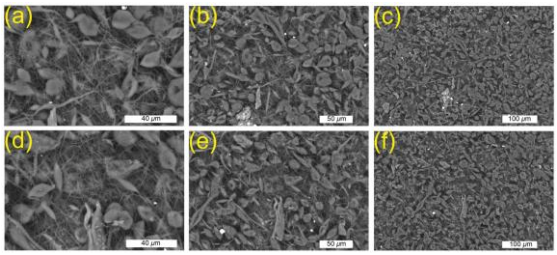

Figure 4. SEM images of electrospun samples at highest (1 wt% a-c), and lowest (10 wt%; d-f) concentrations of strontium aluminate nanoparticles [32]. "Reprinted with permission from {Khattab et al. *Industrial & Engineering Chemistry Research* 2021}. Copyright {2021} *American Chemical Society*."

Figure 5. Photographs of phosphor-immobilized nanofibrous-walled tubes under daytime light (a), ultraviolet source (b), and in the dark (c) [32]. "Reprinted with permission from {Khattab et al. *Industrial & Engineering Chemistry Research* 2021}. Copyright {2021} *American Chemical Society*."

5.2. Rare-earth doped strontion aluminate

$SrAl_2O_4$ was discovered in 1996, Matsuzawa et al established europium and dysprosium ($Eu^{2+}$and Dy^{3+}, respectively) which are rare earth elements and acts as persistent luminescent compounds. By doping the $SrAl_2O_4$(host) with Eu^{2+} and co-doping with Dy^{3+} that leads to the formation of persistent luminescent material. There are another types of rare earths elements acts as dopants (ex: Ce^{3+}, Gd^{3+}, Eu^{2+} Nd^{3+}, $Eu^{3+}Ho^{3+}$and $Dy^{3+}Yb^{3+}$) [100-102]. Some researchers reported that the luminescence behavior for $SrAl_2O_4$ activated with $Eu^{2+}$and Dy^{3+} is due to the monoclinic structure of $SrAl_2O_4$ which is the only structure has luminescence properties [80, 99]. Jia et al. found that the hexagonal structure for $SrAl_2O_4$ has luminescence properties higher than the monoclinic structure [103].

5.3. Synthesis methods

The methods used to synthesize $SrAl_2O_4$-based luminescent material plays a key role in determining the material properties, such as crystal size, luminescent features, and quantum efficiency [104, 105]. The applications of $SrAl_2O_4$ luminescent material require using sub-micron particle size but the large particle size of $SrAl_2O_4$ can't be used. The particle size and microstructure are the two factors that affect on the properties of the luminescent materials. Such as there are advantages obtained from nanosized phosphors there are disadvantages obtained at this size such as the defects during the synthesis conditions, radiationless transitions which decrease the quantum efficiency. Also, the photoluminescent properties affected by the crystal size, there are strong light scattering by nanocrystals for the absorbed excitation light and consequently reduction the emission intensity. Due to the large advantages of luminescent materials in Nano size, the challenge in the field for synthesis this size of materials still exists. There are scientific interests about the methods used to synthesize Eu^{2+}/Dy^{3+} doped $SrAl_2O_4$ phosphors due to its emission in the green spectrum. Many methods are used for synthesis the phosphorescent materials such as chemical [106], co-precipitation, microemulsion [107], sol-gel [108] , combustion [109-111], microwave and laser methods [112] and conventional solid-state method [113]. The conventional solid-state method is the most common one for synthesis these materials because it gives materials with higher brightness and photoluminescence intensity, but there exist some drawbacks by using this method as a following:

(i) It needs a high temperature(>1300 °C).
(ii) The reaction occurs in a long time(>10 hours).
(iii) It consumed a large amount of energy.
(iv) The shape of the produced materials is irregular due to large particle size (some tens of micron) obtained by this method.

Ball milling process (wet-milling) is used in particle size reduction; there are different approaches can be used which expressed in details as a following:

(i) By using absolute ethanol as a milling medium then grinding takes place leading to the reduction of the particle size to 4 μm and decreasing in the luminescence intensity [114-116].
(ii) By using ethyl acetate as a milling medium for nine days, which leads to the formation of fine powder, the photoluminescence properties not affected [82].

Also, dry-milling can be used by different approaches as a following:
(i) By using high energy dry-mill, that leads to agglomeration state.
(ii) By using low energy dry-mill, that leads to the formation of powdered materials with average particle size of 3 μm.
But in these approaches, the particle surface affected during the milling process for decreasing size and that decreases the luminescence intensity [116]. Recently, there is great interest in using the persistent luminescent materials with sub-micron particle size for imaging and security coding applications. The soft chemical methods exhibit an advantage in comparison to the traditional solid-state method in controlling the material structure and its size, but that needs many numbers of synthetic steps which leads to decreasing the luminescence intensity compared to solid-state methods [17-119]. First, thermal treatment occurs at low temperatures (<350 °C) then post-thermal treatment occurs for making improvements in the crystallinity of the powder, consequently that leading to growth in the particle size.

Sol-gel method
In the first step, the gel was exposed heating at 100 °C for 10-24 hours, then the obtained gel powder was heated for 2-16 hours in a reductive environment at 1100-1400 °C by using the solid-state method. There is an approach used for reducing the processing temperature to 1200 °C by addition to B_2O_3 and obtaining the monoclinic structure, this approach was modified by Cordoncillo et al. [108]. Although the reduction of thermal treatment and obtaining more dispersed, homogeneous sized particles by using solid-state method but the photoluminescence behavior is very low compared to these obtained particles [120, 121]. For improvement the intensity of the persistent luminescence the hardening process is performed by making double treatment. However, the obtained particles in submicrometer size (ca. 90 nm) have luminescence with a lifetime 10 minutes and its intensity decreased [122]. Tang and co-workers [107] discovered powders at temperature 900 °C with a particle diameter 60 nm. Their afterglow time is 14 hours. The sol-gel method drawbacks are the following:
(a) The solvent required has the large volume so post hardening treatments are needed.
(b) The preparation of luminescent nanopowders requires controlling the size of the particles and their distribution so the microemulsion method is applied which is used basically in the synthesis of metals, metal oxides, ceramic and sulfur compounds.

Microemulsion method
Microemulsion approach is used in the synthesis of $Y_3Al_5O_{12}:Eu^{3+}$ [123] and $BaMgAl_{10}O_{17}: Eu^{2+}$ nanophosphors [124], that leads to improvement of the crystallinity and reducing in the hardening temperature of the system. There are two approaches for microemulsion method; ordinary approach and reverse approach. These two approaches are used in the preparation of $SrAl_2O_4$: Eu, Dy powders [125]. In an ordinary microemulsion approach, the hardening process and double-thermal treatment are applied to reduce the atmosphere at 1000 and 1100 °C. In reverse microemulsion approach the particles obtained at temperature 900 °C, giving a particle size of 40 nm [126].

Hydrothermal method
The hydrothermal method also used for controlling the particle size and its morphology as sol-gel and microemulsion methods. The hydrothermal method used for the preparation of $SrAl_2O_4$:Eu,Dy powder (needle-like) with particle size of 1 μm by additional thermal treatment at 1200 °C [106]. The phosphors obtained by this method have long-persistent luminescence, but these properties are not as the properties of particles synthesized by the other methods. The previous three methods are complex in their processing, in order to that there are methods can be used without complexity, they require for their processing low thermal treatment, without a post hardening approach. These methods as combustion, laser and microwave methods.

Microwave method
Geng et al. [127] used the microwave method in preparation of $SrAl_2O_4$:Eu, Dy powder; the reaction takes place in 15 min only, the size of the powder obtained is large (408 μm), and the luminescence intensity of the decaying profile extremely decreased as compared to the powder produced by the solid-state method.

Laser method
In the laser method, the preparation reaction of powders can take place in one step. The obtained material has a particle diameter greater than 10 μm [112], and the luminescence lifetime is 3 min only.

Combustion method
This method used in the preparation of inorganic powders [128]. It is fast, has many uses, takes place at low temperature (600 °C), the single doping occurs in one step and there is no importance for the reductive atmosphere [129]. The combustion reaction is an exothermic reaction, the reaction medium is oxidants in the form of the homogeneous solution and it takes place in the attendance of fuel. There are many fuels that can be used such as glycine, carbohydrazide, citric acid, and urea, which are used as initiators in the decomposition reaction. The $SrAl_2O_4$:Eu,Dy particles produced by the combustion

method showed nano(micro)meter size [130, 131]. The obtained particles are agglomerated and formed thin flakes of particles but in the same, these flakes have low density and highly sintered than particles obtained by other methods. These thin flakes with their low density have an important rule that they avoid the high energy produced during the ball milling process which is used to reduce the particle size. For avoiding the post thermal treatment and improvement of the photoluminescence of nanostructured thin flakes (thickness ≤1 μm), the optimization process for the combustion method is required and that occurs by adding nitric acid (oxidizing agent) to a major amount of urea. Also, the reduction of particle size can be obtained by using dry grinding process [110]. On the other hand, Qiu et al. suggested a method takes place in one step to synthesize nanoparticles has size 100 nm and afterglow time about 7h (threshold intensity: 0.32 mCd/m^2) [132]. The molten salt method is used for preparation $SrAl_2O_4$:Eu, Dy, that occurs by using (NaCl/KCl) eutectic mixture, which acts as molten flux [133]. By using this method; the rate of the reaction increases and the formation temperature of $SrAl_2O_4$ decreases compared with the conventional solid-state approach. Consequently, the preparation of $SrAl_2O_4$ prefers low temperature. Submicrometer phosphorescent particles were synthesized at temperature 900 °C for 1 hour. The advantages of the molten salt method compared to other methods in the synthesis of strontium aluminates are:

(a) The multistep processing methods are reduced.

(b) Increasing crystallinity and consequently increasing in the luminescence intensity by using molten flux.

6. Anticounterfeiting applications of inorganic phosphors

Abou-Melha presented recently the preparation of dual-mode anticounterfeiting stamp from photochromic nanocomposite ink containing rare-earth doped aluminate [52]. The composite ink was prepared from a mixture of diammonium phosphate (1% w/w), NH_4OH (1% w/w), polyacrylic acid (15% w/w), distilled water (83%), and strontium aluminate phosphor (0.75% w/w). Another example was reported recently by Khattab el al. [3] as shown in **Figure 6**, demonstrating a simple preparation of photochromic cellulose acetate film integrated with lanthanide-doped phosphor.

El-Newehy et al. reported recently the synthesis of lanthanide-doped strontium aluminum oxide nanoscale particles, which was encapsulated into electrospun polyacrylonitrile nanofibers for anticounterfeiting applications as shown in **Figure 7**. In this study, photochromism was applied as an attractive technique to enhance the anticounterfeiting of commercial produces. The provided photochromic nanofibrous films showed transparency, photostability, stretchability, and flexibility at low-cost. This strategy can be reported as an efficient method toward the preparation of anticounterfeiting materials toward a market of better social and economic values [35].

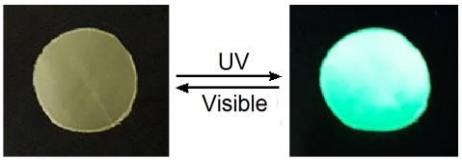

Figure 6. Photochromism of cellulose acetate photochromic nanocomposite film containing rare-earth doped aluminate, displaying color change from colorless under daytime light to green emission under ultraviolet rays [3]. "Reprinted with permission from {Khattab et al. *Luminescence* 2021}. Copyright {2021} *Wiley*."

Figure 7. Photographic images of photochromic electrospun nanofibrous film, demonstrating a color change from colorless under visible light to green under ultraviolet lights [35]. "Reprinted with permission from {El-Newehy et al. *Luminescence* 2022}. Copyright {2021} *Wiley*."

Although there exist many methods, as shown above, used for the preparation of phosphorescent nanopowders but these methods are primitive methods. $SrAl_2O_4$:Eu, Dy phosphorescent material is the most common micrometric particle used in commercial application, and it has been prepared by conventional solid-state method. The materials prepared by the traditional method at high temperature show many characteristics. There are many patent studies about long persistent phosphors, which are associated with aluminate hosts. There are two factors affects the cost of the final product:

(a) Using high temperature in the synthesis process (1300-1500 °C).

(b) Using long processing time.

Thus, the conventional method needs to reduce these two factors for obtaining low cost, high luminescent products. This method aimed to obtain high particle distribution which can overcome the high-cost methodologies and that achieved by using the rare earth materials and grinding steps. The researchers focused their studies on preparing rare earth(raw) materials which can be used at low temperatures and short processing time to obtain a reduction of the final price [134-138]. A preparation method was introduced for persistent phosphor with chemical structure MAl_2O_4:Eu by recycling the wastes of rare earth aluminate [139]. By this method, the low-cost

product was obtained. The obtained particles mentioned above have the size in between 10-1000 μm. There is importance for synthesizing particles have the size in the sub-micrometer scale because this size is still required. So, General Electric Group showed the possibility of using the sol-gel method for synthesizing nanophosphors based on strontium aluminates which have a size in between 100-900 nm. They feign the using of this method for synthesizing different phosphors but they don't give results about the strontium aluminates [140]. Hangzhou Truth-Chem Co. Ltd.is other Chinese company which has the same importance of working in this field [141] which gives the same products obtained through the development occurs by Chinese companies. In general, all manufacturers prepared different long-lasting luminescence powders with different qualities that have a particle size about 100 μm. The alkaline earth aluminates are the main component of the green phosphorescent powders. The silicate aluminate oxides are the main component of orange-yellow phosphorescent powders. Improvement the water stability of the phosphors is very important; this can take place by using encapsulation methods which improve the water-resistance of $SrAl_2O_4$ without remarkably decreasing in its optical properties. Luminescent materials which have fast response toward an external stimulation, it undergoes to great interest. According to the type of the external stimuli, these materials have classified. If the stimulation occurs by photoexcitation, and consequently the light emission phenomenon called photoluminescence. The luminescence phenomenon as mentioned above classified into two types; fluorescence which has short lifetime for the emitted light (10^{-9}–10^{-7}s) and phosphorescence which have a long lifetime for the emitted light last for minutes to hours. There is a special interest in luminescent materials which gives green emission, this special interest is due to the eye sensitivity function (luminous efficiency function). The vision systems classified into three different types as a following:

(i) Photopic vision; is the human vision in a high level of illumination of the surrounding medium (e.g. the vision during the daylight, the luminescence greater than 3 cd/m^2).

(ii) Scotopic vision; is the human vision in the low level of illumination of the surrounding medium, it occurs at 507nm (e.g. The vision at night, the luminescence less than0.003 cd/m^2).

(iii) Mesopic vision; is the human vision in intermediate level of illumination of the surrounding medium.

Thus, it has been interesting to develop materials that have emission in the green spectral region and take in mind the long emission lifetime is required also due to the wide range of applications [142, 143]. There exist many green-emitting materials that have been studied. The research concentrated on SrAl2O4 doped with eropium and dysprosium due to its good stability and high phosphorescence properties [144-147]. Due to these advantages, it has a broad range of applications like afterglow luminous paints which one of their uses in inks, ceramics, emergency marks, and in textile such as security textile. Also, it shares in the advanced technologies such as lighting, sensors that used for detecting the dangerous chemicals and biological agents, imaging (invitro and invivo) [148], LEDs, security encoding. Therefore, we can say that this smart luminescent material enters in many fields such as displays, defense, medicine, the military also in our daily life in cosmetic and dermatological compositions [149-151]. The idea in the smart high ways was suggested by Dutch companies, they processed the paints by mixing them with photoluminescent powder absorbs the sunlight during the day, and then emits this light and glow for more than 10 hours in the dark that leads to lighting the road without cost, however, the long afterglow $SrAl_2O_4$:Eu, Dy is used for making enhancement the performance [58]. These approaches lead to saving the energy in signage, buildings without violation of safety rules. There are numerous properties for the white light-emitting diodes(WLEDs); its luminous efficiency is high, has the ability for saving energy, has a long lifetime and more applicable [152]. A combination of three types of phosphors gives three types of emission (red, green and blue). e.g. Y_2O_2S: Eu, Ti, Mg→red emission, $CaAl_2O_4$:Eu, Nd→blue emission, and $SrAl_2O_4$:Eu,Dy→green emission [153-156]. The luminescence efficiency for the phosphorescence materials in the above two methods is low, so there is an interest in discovering phosphors that have high luminescence efficiency by using UV-LED or blue-LED as an excitation light source to obtain warm lighting on a level of safety and comfort. In recent times, $SrAl_2O_4$, doped with Dy^{3+}, Ce^{3+} was suggested as a source of white light obtained by a direct emission [157, 158]. The UV-LEDs have low cost and this is the reason for using them as an excitation light source for phosphors to yield white light, also there exist another method for obtaining white light is by using Ce^{3+}, Tb^{3+}or Ce^{3+}, Mn^{2+} as a doping materials for the hosts, and by using Dy^{3+} as a doping material for $ZnWO_4$, $Gd_2Al_5O_{12}$ [159, 160]. There is a challenge for synthesizing phosphors with low cost and high purity. So for this reason, aluminate-based materials are used, especially, the strontium aluminates which are high efficient hosts that give wideband emission when doped with lanthanide elements. By doping $SrAl_2O_4$ with lanthanides then this system was exposed to UV radiation that makes it exhibits long last phosphorescence (persistent luminescence). Recently, by exposure to the $SrAl_2O_4$:Eu, Dy to X-ray radiation

that leads to the occurrence of significant emission so can be easily used as scintillators (radiation detector).

7. Limitations and future trends

Due to the importance of $SrAl_2O_4$:Eu, Dy luminescent materials and its sharing in numerous applications as mentioned above, the conventional methods used for synthesizing these materials leads to formation of materials has large particle size (≥ 20 μm)and consequently inhomogeneous particle distribution, so there is challenge to searching for a new technologies and processing methods which carry out to prepare these luminescent materials and make them able to introduce many applications which will be applied in near future. There are requirements for using these materials in demanding applications:

(a) The material powder must be in a sub-micrometer size.

(b) The material powder must be more white and not have yellow color. Because of this yellow-colored material applied in applications as an example in emergency signs, the color form undesired visual impact effects on the artistic requirements. Synthesis of particles having a size in the sub-micrometer scale, there are two approaches can be applied, including the milling process for the bulk material, and synthesizing these submicron particles directly. There is no milling process suitable for using until our time, the milling process has disadvantages, it produces high energy during the milling process leading to formation of particle amorphous surface and that decrease the particle reactivity and consequently decreasing its luminosity; at the same time by using dry milling process which decrease the energy obtained and consequently the crystallinity and the functional luminescent properties of the obtained particle not affected. But the two cases fail to obtain particles ≤ 1 μm. Also, by using the direct methods for synthesizing the submicron particles that lead to a large increase in the surface energy and that makes distortion for the particle surface and effects on its crystallinity structure, make a change in the crystal field surrounding the dopants sites (Dy^{3+} and Eu^{2+}) leading to decreasing in the photoluminescence properties. The morphology of the nanophosphor particles is responsible for their final properties; the particle structure of nano phosphor is usually spherical. So, the nanostructure increase and improve the efficiency of the phosphorescent materials. There is required development for approaches which needed for synthesizing well-defined morphologies. $BaAl_2O_4$:Eu, Dy nanotubes were synthesized by a combination of the hydrothermal approach with the post hardening technique at 1300 °C [161]. The obtained particles have diameter 100-300nm and length greater than ten of a micrometer. Nevertheless, the afterglow decay rate for the nanostructured $BaAl_2O_4$: Eu, Dy is faster than its bulk form. The $SrAl_2O_4$:Eu, Dy, Ce with a diameter of 90 nm, and length of 650 nm was synthesized by hardening at 1300 °C, post hardening at 1200 °C, and mechanical deposition for the prepared particles on templates of SiO_2 and Al_2O_3 [162]. $Sr_2MgSi_2O_7$: Eu, Dy nanotubes with diameter 70-80 nm was synthesized by using the anodic alumina oxide [163-167]. $SrAl_2O_4$:Eu, Dy Nanosheets with 100nm width and 1 μm length were synthesized by using the hydrothermal method in an autoclave at temperature 160 °C for 24 hours then the post hardening takes place at 1300 °C for 2 hours under active carbon which acts as reducing atmosphere. But the afterglow of $SrAl_2O_4$:Eu, Dy nanosheets decays faster than the afterglow of the commercial powders, which synthesized by the solid-state method [168]. The phosphor structure was determined according to the type of application used it.

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